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Electrochemical Strain Microscopy of Li-ion battery cathodes

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Electrochemical strain microscopy (ESM) can provide useful information on the ionic processes in materials at the local scale. This is especially important for ever growing applications of Li-batteries whose current performance is limited by various intrinsic and extrinsic degradation mechanisms. In this context, ESM is indispensable because it helps uncovering these mechanisms on the nanoscale. However, the ESM method used so far [1] has been only qualitative due to multiple contributions to the measured ESM signal.

In this work, we provide a viable approach for the local probing of ionic concentration and diffusion coefficients based on the low frequency dependence of the ESM signal. A theoretical basis considering the dynamic behavior of ion migration and relaxation and change of ion concentration profiles under the action of the electric field of the ESM tip is developed [2]. We argue that several parasitic contributions to the ESM signal recently discussed in the literature [3] can be thus eliminated. The analysis of ESM images using the proposed approach allows a quantitative mapping of the ionic diffusion coefficients and concentration in ionic conductors (Fig. 1). The results are validated on Li-battery cathodes ($LiMn_2O_4$) extracted from commercial Li-batteries and provide novel possibilities for their development and further insights into the mechanisms of their degradation after prolonged use. The ESM results are complemented by the micro Raman microscopy investigations [4] that confirm the conclusions provided by ESM.

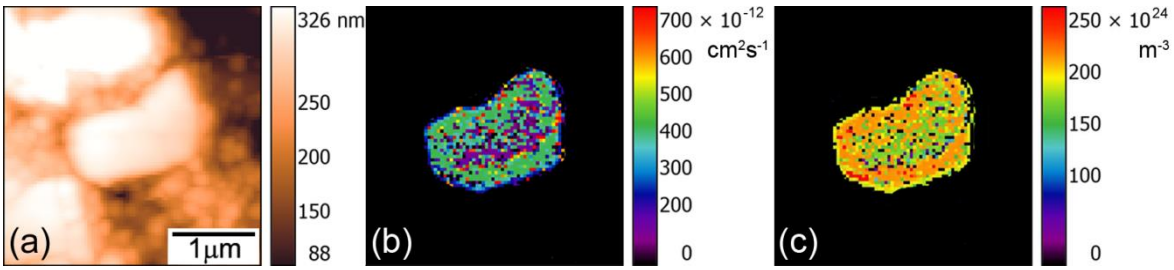

Figure 1. Topography (a), diffusion coefficient (b) and ionic concentration (c) maps of the $LiMn_2O_4$ cathode extracted from commercial battery.

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